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CENTRAL INTELLIGENCE AGENCY
INFORMATION FROM
FOREIGN DOCUMENTS OR RADIO BROADCASTS

REPORT

CD NO.

50X1-HUM

COUNTRY USSR

SUBJECT Scientific - Insecticides

HOW PUBLISHED Monthly periodical

WHERE PUBLISHED Moscow

DATE PUBLISHED Jan 1949

LANGUAGE Russian

DATE OF INFORMATION 1949

DATE DIST. 16 Nov 1949

NO. OF PAGES 8

SUPPLEMENT TO REPORT NO.

THIS IS UNEVALUATED INFORMATION

SOURCE Zhurnal Prikladnoy Khimii, Vol XXII, No 1.

PHYSICOCHEMICAL PROPERTIES OF CALCIUM ARSENATES

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[Figures are appended.]

Industrial calcium arsenate used as an enterotropic insecticide is a basic calcium salt of orthoarsenic acid. The exact composition and structure of industrial samples is unknown. The molar ratio $CaO : As_2O_5$ varies from 3.3 to 3.7 in various samples. While conducting physicochemical studies in the field of calcium arsenates, we developed a method for obtaining neutral and basic calcium salts of orthoarsenic acid. As a starting agent we used arsenic acid and a calcium hydroxide solution instead of suspensions. With the use of the calcium hydroxide solution, we obtained in pure form the following crystallic compounds: $4CaO \cdot As_2O_5 \cdot 5H_2O$, pentahydrate of tetracalcium-arsenate and $3CaO \cdot As_2O_5 \cdot 10H_2O$, decahydrate of tricalcium-arsenate. The first is made up of rectangular prisms and the second, of rhombic flakes.

While preparing the individual compounds and also in studying their chemical properties, we noted that their water suspensions have quite different properties. Thus, a suspension of $4CaO \cdot As_2O_5 \cdot 5H_2O$ in the ratio of 0.1 gm of the substance to 25 ml of water has an alkaline reaction (pH9.6); and in the titration of such a suspension with a 0.02 N HCl solution in the presence of phenolphthalein, the alkaline coloring of the indicator increased continuously. Complete neutralization took place only when about 12 - 15 percent of the calcium oxide was titrated back by the acid. On the other hand, a water suspension of a solid solution of calcium hydroxide in dihydrate of tricalcium-arsenate with molar ratio $CaO : As_2O_5$ equal to 3.8 under the very same conditions has pH 8.6, and the phenolphthalein coloring disappears after titrating back only 1 - 2 percent CaO.

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Water suspensions of $3CaO \cdot As_2O_5 \cdot 10H_2O$ and $3CaO \cdot As_2O_5 \cdot 2H_2O$ also have different properties. Suspensions of $3CaO \cdot As_2O_5 \cdot 10H_2O$ have pH 9.1. In titrating a suspension with 0.02 N HCl solution in the presence of phenolphthalein, neutralization took place only after 5 - 6 percent of CaO was titrated back by the acid. Suspensions of $CaO \cdot As_2O_5 \cdot 2H_2O$ have pH 8.3, and neutralization of the suspension occurred after adding several drops of a 0.02 N HCl solution.

These observations were made on numerous samples, the phase composition of which had been previously investigated.

The results of titrating water suspensions of various samples with a 0.02 N HCl solution and the pH determinations for the solutions are shown in Table 1. It should be noted that, in titrating suspensions from $4CaO \cdot As_2O_5 \cdot 5H_2O$ or $3CaO \cdot As_2O_5 \cdot 10H_2O$, the greater part of the CaO was titrated back in 40 - 60 minutes and only 1 percent of CaO in 24 hours. In the titration of suspensions of $3CaO \cdot As_2O_5 \cdot 2H_2O$ and solid solutions, the time of complete neutralization was 70 - 80 hours. The results show that the difference in the behavior of water suspensions of calcium arsenate samples is not chance, but follows a definite pattern: suspensions from $4CaO \cdot As_2O_5 \cdot 5H_2O$ or $3CaO \cdot As_2O_5 \cdot 10H_2O$ yield a neutral reaction with phenophthalein only after adding 0.02 N HCl solution in the amount necessary to reduce the solid phase to a composition of approximately $2.5CaO \cdot As_2O_5$ (calculated). Suspensions of $3CaO \cdot As_2O_5 \cdot 2H_2O$ or solid solutions have pH 8.3 - 8.6, and therefore the neutralization takes place after the addition of very small quantities of the 0.02 N HCl solution.

It is possible that this difference in the properties of the compounds should be ascribed to the structure of the compound's crystal lattice. We checked the "solubility" of the compounds having different pH values (solubility is set in quotes because absolute solubility is not being considered).

Compositions and "Solubility" Curves

The tests were conducted for pH values ranging from 7.5 to 10 by the following method: A weighed portion of the sample (0.1 g) was placed in a cylindrical vessel (capacity - 100 ml). Then 50 ml of a standard buffer solution were poured in the vessel. The solubility of each sample was determined at four points with pH values equal to 7.3, 8.2, 9.2, and 10. The vessels were placed in a water thermostat in which they were rotated continuously for 6 hours. Then the vessels were left undisturbed for 14 hours and again rotated for 4 hours. The thermostat temperature was 25 degrees. The pH values and the As_2O_5 content were determined in filtrates by the iodometric method. The solubility was expressed mg-equivalents of As_2O_5 per liter. The pH value of the filtrates was determined by the colorimetric indicator method.

The buffer solution was prepared from boric acid, borax, KOH, and KCl. We intentionally refrained from using phosphoric acid salts, remembering previous references to excellent results for solubility obtained in the region of high pH values due to the low solubility of calcium phosphate which forms under these conditions.

Table 1. Results of Titrating Suspensions from 0.1 g of the Substance in 25 ml of H_2O in the Presence of Phenophthalein.

No of Samples	CaO/As_2O_5 by Chemical Analysis	Chemical Formula	Titration of Suspensions With Phenophthalein		Initial Value of Suspensions' pH Value
			0.02 N HCL solution (ml)	CaO (%)	
87	4.0	$4CaO \cdot As_2O_5 \cdot 5H_2O$	25.3	14.2	9.6
50'	4.0		23.2	13.0	9.6
65	4.0		25.6	14.3	
66	4.0		20.75	11.6	9.6
67	4.0		21.1	11.8	9.6

(Contd)

No of Samples	CaO/As_2O_5 by Chemical Analysis	Chemical Formula	Titration of Suspensions With Phenophthalein		Initial Value of Suspensions' pH Value
			0.02 N HCl solution (ml)	CaO (%)	
48	3.0	$3CaO \cdot As_2O_5 \cdot 10H_2O$	9.0	5.0	9.1
32	3.0	$3CaO \cdot As_2O_5 \cdot 10H_2O$	10.0	5.6	---
123	3.0	$3CaO \cdot As_2O_5 \cdot 2H_2O$	0.7	0.4	8.3
53	3.4	Solid solutions	1.0	0.56	---
64	3.6		2.5	1.4	8.5
63	3.5		2.4	1.3	--
57	3.8		3.1	1.74	8.6
46	3.7		1.0	0.56	
112	3.3		1.5	0.84	
113	3.7		2.3	1.29	
114	3.5		2.0	1.12	

Table 2. Results of Determining the "Solubility" of Calcium Arsenate Samples

No of Samples	Composition	"Solubility" in Buffer Media in Mg-equivalents of As_2O_5 per Liter							
		pH	mg eq As_2O_5	pH	mg eq As_2O_5	pH	mg eq As_2O_5	pH	mg eq As_2O_5
48	$3CaO \cdot As_2O_5 \cdot 10H_2O$	7.5	13.0	8.2	8.2	9.3	4.7	10	4.1
50	$3CaO \cdot As_2O_5 \cdot 10H_2O$	7.5	13.5	8.2	10.0	9.2	5.4	10	4.0
87	$4CaO \cdot As_2O_5 \cdot 5H_2O$	7.8	12.5	8.2	10.6	9.4	5.3	10	2.7
65	$4CaO \cdot As_2O_5 \cdot 5H_2O$	7.9	13.4	8.2	10.6	9.3	5.6	10	3.4
69	$4CaO \cdot As_2O_5 \cdot 5H_2O$	7.9	12.6	8.2	11.0	9.4	5.9	10	3.5
123	$3CaO \cdot As_2O_5 \cdot 2H_2O$	7.4	6.4	8.1	3.4	9.2	2.3	10	1.6
46	$CaO:As_2O_5=3.2$ Solid solutions	7.5	4.1	8.1	1.85	9.3	0.9	10	0.85
112	$CaO:As_2O_5=3.28$	7.5	3.9	8.2	2.2	9.4	0.9	10	0.77
53	$CaO:As_2O_5=3.4$	7.5	3.2	8.1	1.2	9.2	1.1	10	0.65
63	$CaO:As_2O_5=3.53$	7.5	3.8	8.1	1.3	9.2	0.8	10	0.4
74	$CaO:As_2O_5=3.6$	7.5	3.4	8.1	1.0	9.2	0.3	10	0.3
57	$CaO:As_2O_5=3.8$	7.5	3.3	8.2	1.2	9.2	0.3	10	0.1

The results of determining the "solubility" of calcium arsenate samples are presented in Table 2 and Figure 1.

As seen from the results, the "solubility" curves for $4CaO \cdot As_2O_5 \cdot 5H_2O$ and $3CaO \cdot As_2O_5 \cdot 10H_2O$ are very close and are much higher than the "solubility" curves for $3CaO \cdot As_2O_5 \cdot 2H_2O$ and are solid solutions. The solubility of the latter is low and has a tendency to decrease with increase in the molar ratio CaO/As_2O_5 in the solid solution.

The Connection of the Chemical Properties and "Solubility" Curves With the Structure of Calcium Salts of Orthoarsenic Acid.

It is possible to separate the compounds under study into two types on the basis of the chemical properties and solubility curves of neutral and basic calcium salts of orthoarsenic acid.

The first type includes:

$4CaO \cdot As_2O_5 \cdot 5H_2O$ - high "solubility" in the pH range 7.5-10: water suspension has pH 9.6; neutralization by acid indicated by phenophthalein takes place after titrating back approximately 14% CaO;

$3CaO \cdot As_2O_5 \cdot 10H_2O$ - high "solubility" in the pH range 7.5-10: water suspension has pH 9.1; neutralization of acid takes place after titrating back approximately 5-6% CaO.

The second type includes:

$3CaO \cdot As_2O_5 \cdot 2H_2O$ and solid solutions of calcium hydroxide in it with a $CaO : As_2O_5$ ratio equal to 3.2-3.8; low solubility in the pH range 7.5-10; water suspension has pH 8.3-8.6; neutralization takes place after titrating back approximately 1-2% CaO.

On the other hand, it is known that chemical analysis of samples by the percentage content of CaO and As_2O_5 and calculation of the molar ratio $CaO : As_2O_5$ in a substance are not sufficient to determine the phase composition of the compound. X-ray analysis is not always obtainable and furthermore Debye graphs cannot be obtained for many finely dispersed samples. Therefore, we attempted to use the characteristics of the above-listed individual compounds as a method for determining the phase composition of salts and their mixtures.

The solubility curves are shown in Figure 2. The results of determining the phase composition of various samples by titration of their suspensions and "solubility" curves are shown in Table 3.

Table 3

No	CaO : As_2O_5	Quality of CaO in Suspension	pH	As_2O_5 mg eq	pH	As_2O_5 mg eq	pH	As_2O_5 mg eq	pH	As_2O_5 mg eq	Composition
51	3.72	1.2	7.5	3.3	8.1	1.35	9.2	0.55	10	0.4	Solid solution
75	3.02	3.92	7.5	7.55	8.2	5.8	9.3	3.1	10	2.3	Mixture of $3CaO \cdot As_2O_5 \cdot 10H_2O$ and $3CaO \cdot As_2O_5 \cdot 2H_2O$
76	3.4	9.70	7.5	4.45	8.1	1.35	9.3	0.8	10	0.7	Solid solution
78	3.6	2.52	7.5	3.35	8.1	1.15	9.2	0.6	10	0.45	Solid solution
52	3.85	9.42	7.7	7.10	8.2	7.0	9.3	5.2	10	2.2	Mixture of $4CaO \cdot As_2O_5 \cdot 5H_2O$ with dihydrate or solid solution
83	3.35	4.48	7.5	7.45	8.1	4.9	9.2	3.05	10	2.8	Mixture of $3CaO \cdot As_2O_5 \cdot 10H_2O$ with solid solution
59	3.93	7.84	7.6	5.10	8.2	4.9	9.2	4.9	10	3.4	Mixture of $4CaO \cdot As_2O_5 \cdot 5H_2O$ with solid solution
62	4.1	9.4	7.9	13.2	8.2	10.8	9.2	6.4	10	3.8	$4CaO \cdot As_2O_5 \cdot 5H_2O$ and a small admixture of $3CaO \cdot As_2O_5 \cdot 10H_2O$
54	3.8	5.04	7.45	3.6	8.1	2.9	9.2	2.8	10	2.6	Solid solution and a small admixture of $3CaO \cdot As_2O_5 \cdot 10H_2O$
58	4.0	15.0	7.9	11.7	8.2	10.8	9.3	6.1	10	3.4	$4CaO \cdot As_2O_5 \cdot 5H_2O$
57	3.85	1.1	7.5	3.3	8.3	1.2	9.2	0.85	10	0.1	Solid solution
71	9.93	15	7.9	13.63	8.2	11.1	9.2	6.1	10	3.0	$4CaO \cdot As_2O_5 \cdot 5H_2O$

$4CaO \cdot As_2O_5 \cdot 5H_2O$, $3CaO \cdot As_2O_5 \cdot 10H_2O$, $3CaO \cdot As_2O_5 \cdot 2H_2O$ and solid solutions were taken as standards for comparison.

From Table 3 it is seen that it is not always necessary to record solubility curves. Sometimes it is sufficient to titrate the suspension with a 0.02 N HCl solution. Actually, if the percent of CaO is less than 2 according to the results of titration with phenolphthalein, then it is possible to say that the compound belongs to the second type -- i.e. is $3CaO \cdot As_2O_5 \cdot 2H_2O$ or a solid solution, for example, samples 51 and 57.

By the same token, if titration of the suspension yields a percent of CaO close to 15, then without the solubility curves it is possible to conclude that the sample is $4CaO \cdot As_2O_5 \cdot 5H_2O$, for example, samples 58 and 71.

We introduce several examples in which the CaO percent ranges from 2 to 15 according to titration.

Sample 75 -- CaO - 3.92 percent, $CaO:As_2O_5$ ratio 3.02 according to chemical analysis. "Solubility" average for pH values 7.5-10; this means that this sample is a mechanical mixture of $3CaO \cdot As_2O_5 \cdot 10H_2O$ and $3CaO \cdot As_2O_5 \cdot 2H_2O$.

Sample 59 -- CaO - 7.84 percent, $CaO:As_2O_5$ ratio 3.93. "Solubility" average. Consequently, the sample is a mixture of $4CaO \cdot As_2O_5 \cdot 5H_2O$ with a solid solution.

Sample 52 -- CaO - 9.42 percent, $CaO:As_2O_5$ ratio 3.85. "Solubility" average. Obviously, this is a mixture of $4CaO \cdot As_2O_5 \cdot 5H_2O$ and a solid solution.

Sample 83 -- CaO - 4.48 percent, $CaO:As_2O_5$ ratio 3.35. "Solubility" average. The sample is a mixture of approximately 70 percent $3CaO \cdot As_2O_5 \cdot 10H_2O$ and approximately 30 percent solid solution.

If this substance had been a mixture of approximately 30 percent $4CaO \cdot As_2O_5 \cdot 5H_2O$ and 70 percent $3CaO \cdot As_2O_5 \cdot 2H_2O$, then its solubility would have been lower.

In our physicochemical investigation we often utilized this method to determine the phase composition of intermediate and sometimes terminal phases. In a majority of cases, this method was of invaluable assistance in our work.

It is obvious that there must not be free calcium oxide in these substances. If there is, it is necessary to determine the content of free calcium oxide by the benzoin method (in an alcohol solution) and allow for it in the result obtained by the titration of the solution with a 0.02 N HCl solution in the presence of phenophthalein. In this case, a "solubility" curve should be recorded.

Conclusions

1. Two types of compounds were established after studying the properties of basic and neutral calcium salts of orthoarsenic acid.

Type I. -- $4CaO \cdot As_2O_5 \cdot 5H_2O$, and $3CaO \cdot As_2O_5 \cdot 10H_2O$. Water suspensions have pH values of 9.6 and 9.1, respectively; neutralization of suspensions by acid indicated by phenophthalein takes place for those compounds whose basicity reduces to a $Ca:As_2O_5$ ratio equal approximately to 2.7 - 2.5 in the solid phase. Both compounds are highly soluble in the pH range 7.5 - 10; consequently, they are highly toxic.

Type II. -- $3CaO\ As_2O_5 \cdot 2H_2O$ and solid solutions. Water suspensions have pH values of 8.3 - 8.6 and are highly titrated by acid in the presence of phenolphthalein. "Solubility" is relatively low.

It is possible that the marked difference in the properties of these two types of compounds is due to the different structure of the crystal lattice.

2. An attempt was made to utilize the results obtained from the "solubility" curves and titration of suspensions of the individual compounds as a method for determining the phase composition of unknown samples and mixtures.

3. The data obtained makes it possible to obtain basic calcium salts of orthoarsenic acids which, due to their solubility in the alkaline range, are much more toxic than industrial samples now used.

[Appended figures follow.]

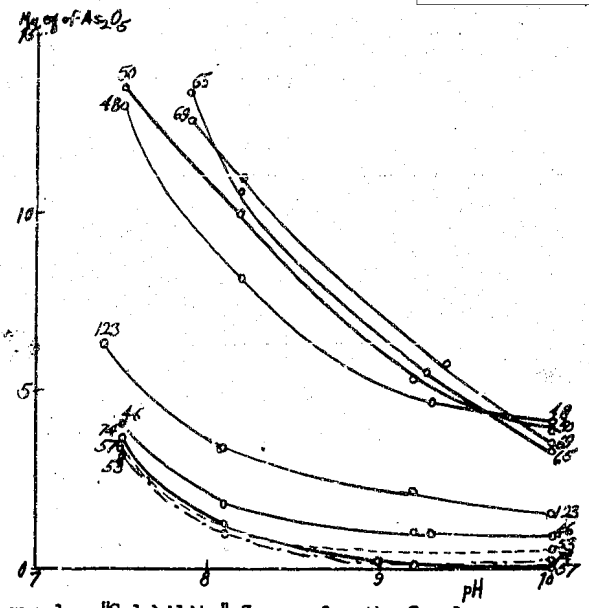

Figure 1. "Solubility" Curves for the Samples:
46, 48, 50, 53, 57, 65, 69, 74, 123

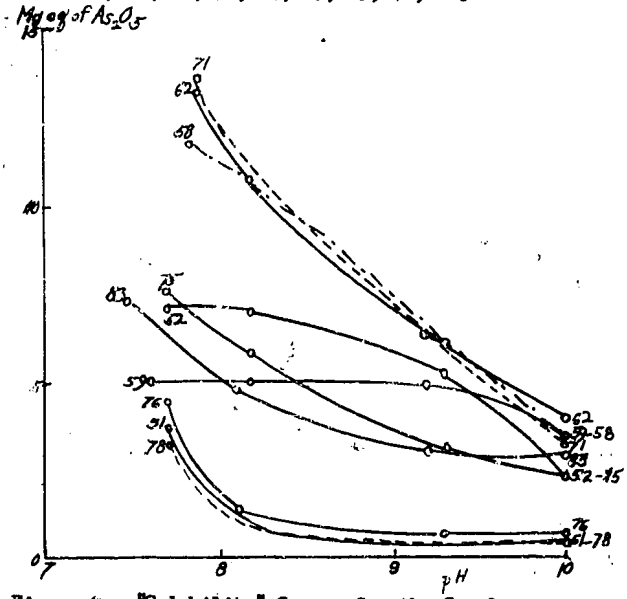

Figure 2. "Solubility" Curves for the Samples:
51, 52, 58, 59, 62, 71, 75, 76, 78, 83

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